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Anti-Polarity in Ideal $BiMnO_3$

Pio Baettig,[†,‡,§] Ram Seshadri,[†] and Nicola A. Spaldin*,[†]

Materials Department, University of California, Santa Barbara, California 93106-5050, Chemistry Department, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland, and Department of Quantum Matter, ADSM, Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshimashi 739-8530, Japan

Perovskite-structure bismuth manganite has been the focus of recent attention because of its potential as a multiferroic material exhibiting simultaneous ferromagnetism and ferroelectricity. Indeed, early reports of ferromagnetism[1−3] have been confirmed by modern studies,[4,5] and the ferromagnetic ordering temperature of ∼100 K and substantial magnetization of ∼3.2 μ_B per formula unit are now well-established. In addition, two recent structure determinations using room temperature[6] and low temperature[7] powder neutron diffraction found a noncentrosymmetric *C*2 space group, which permits the existence of ferroelectricity. Subsequently, ferroelectric hysteresis loops were measured on polycrystalline and thin-film samples,[8] and second harmonic response, indicative of polarity, was reported in $BiMnO_3$ thin films.[9]

The polar behavior has been rationalized, using first-principles density functional calculations, in terms of the *stereochemical activity* of the Bi^{3+} $6s^2$ lone pair.[10−12] In stereochemically lone-pair-active cations, off-centering toward a neighboring anion (or anions) is accompanied by charge transfer into formally empty cation states (in this case Bi 6p orbitals). The resulting covalent bond formation stabilizes the off-centering and produces characteristic lobe-shaped "lone pairs" around the cation (see for example, Figure 10 of ref 11). Although early first-principles calculations for the high symmetry cubic structure found an unstable zone-center phonon suggestive of ferroelectric behavior,[10] subsequent calculations for the experimentally reported structure[12] showed that the local Bi−O displacements in fact anti-align. The resulting structure is almost antiferroelectric, with small inequivalences between sites yielding a *ferri*-electric arrangement with a net polarization. The off-centering of the Bi ions also introduces a strain into the lattice which is responsible for the unusual orbital ordering that results in ferromagnetism.[6,7,12]

The seemingly consistent picture of ferro- or ferri-electricity and ferromagnetism in $BiMnO_3$ was recently called into question, however, by an analysis of the related material, $BiScO_3$.[13] $BiScO_3$ is not a multiferroic (the formally trivalent Sc^{3+} ion is nonmagnetic) and is therefore a more straightforward system for studying Bi lone pair activity in perovskite-structure oxides, without the accompanying complication of magnetism. $BiScO_3$ was found to have the same monoclinic crystal system as $BiMnO_3$, with similar lattice parameters. However, both X-ray powder and electron diffraction reflections yielded unambiguously a centrosymmetric *C*2/*c* structure. As expected, Rietveld analysis of the neutron powder diffraction data within this *C*2/*c* space group gave typical positive thermal parameters, small estimated standard deviations for the fractional atomic coordinates and thermal parameters, and appropriate *R* factors. Interestingly, Rietveld refinement within the *C*2 space group gave slightly smaller *R* factors (a result of the larger number of structural parameters in *C*2) but unphysically negative thermal parameters for two of the oxygen atoms and estimated standard deviations 1 order of magnitude larger than those obtained within *C*2/*c*. The negative thermal parameters and large estimated standard deviations are indicators that a center of symmetry has been missed. The authors of ref 13 pointed out that similarly large estimated standard deviations occurred in the earlier refinements of $BiMnO_3$ within the *C*2 space group[6,7] and suggested that $BiMnO_3$ might in fact be centrosymmetric. Subsequently, the same group used selected area electron diffraction, convergent beam electron diffraction, and Rietveld analysis of neutron diffraction data to study polycrystalline $BiMnO_3$ directly.[14] Their data indicated that $BiMnO_3$ crystallizes in the centrosymmetric *C*2/*c* space group. In addition, Montanari et al. recently found that the actual structure depends sensitively on the oxygen stoichiometry[15,16] and used neutron studies on polycrystalline samples as a function of magnetic field and temperature to suggest that the ideal structure is centrosymmetric *C*2/*c*.[17]

In an effort to resolve this controversy, here we use the LDA+*U* method of density functional theory to perform the first full computational structural optimization of $BiMnO_3$ and to compare the structure and properties of our calculated lowest energy structure to the experimentally reported structures. We find that, although the two reported *C*2 structures are indeed polar, they are in fact higher in energy than a closely related centrosymmetric *C*2/*c* structure with zero polarization. Our result is consistent with the recent structural work on polycrystalline bulk samples but cannot explain the earlier ferroelectric hysteresis loops or second harmonic signals.

First we compare the energies and polarizations of the experimental structures reported by Atou and co-workers[6] and dos Santos and co-workers[7] (we refer to these as the "Atou" and "dos Santos" structures in the following; note that the *x* position of O(5) in the dos Santos structure is 0.349 not 0.300 as reported in ref 7[12]). Our calculations are performed using the projector augmented wave (PAW) method[18,19] of density functional theory[20,21] as implemented in the VASP code.[22,23] The exchange-correlation functional is treated using the LDA+*U* model in the around mean field limit[24] with a U_{eff} (=$U - J$) of 5.2 eV on the Mn d orbitals. We use the default VASP PAW potentials (Bi_d, Mn_pv, O) and calculate the charge densities using a Γ-centered 4 × 4 × 2 k-point mesh and an energy cutoff of 450 eV. Polarizations are extracted using the Berry phase method[25−28] with a sampling of 10 k-points per string in the direction of polarization. We find that the two structures differ considerably in their total energies and polarizations, with the Atou structure having a substantial polarization of 18.96 $\mu C/cm^2$, compared with a small value of 0.9 $\mu C/cm^2$ for the dos Santos structure. (This latter value is comparable to an earlier report of 0.52 $\mu C/cm^2$ calculated for the same structure using the full-potential linear augmented plane wave approach,[12] $U = 8$ eV and $J = 1.06$

[†] University of California, Santa Barbara.
[‡] University of Fribourg.
[§] Hiroshima University.

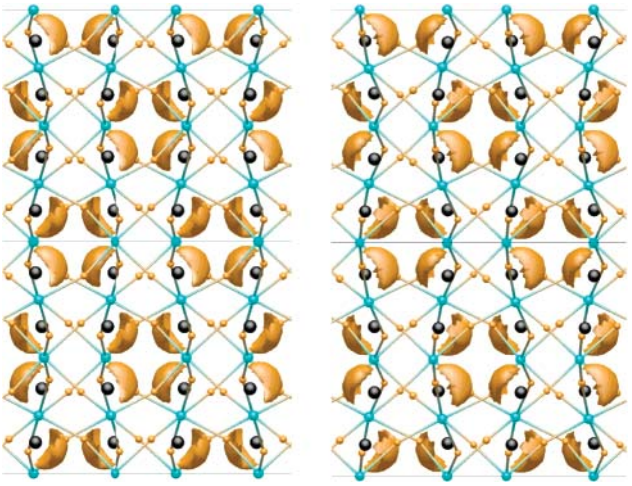

Figure 1. Calculated electron localization functions for the structurally optimized theoretical *C*2/*c* structure (left) and the experimentally reported "Atou" structure of ref 6 (right). Visualizations were performed with the Stuttgart TB-LMTO-ASA code, as described previously.[11] The electron localization function (ELF) isosurfaces are visualized for a value of 0.8. The yellow lobes are the lone pairs on the black Bi ions. The structures are oriented with the monoclinic *c*-axis out of the page, the *a*-axis vertically, and the polar *b*-axis to the right (the monoclinic *a*, *b*, and *c* axes correspond to the [11$\bar{2}$], [$\bar{1}$10] and [112] perovskite pseudocubic directions respectively). Note that in the *C*2/*c* structure the lone pairs cancel perfectly, whereas in the Atou structure there is imperfect cancellation leading to a small net polarization along *b*.

eV.) The smaller-polarization dos Santos structure is lower in energy than the Atou structure by 0.1 eV per five-atom formula unit.

Next we perform full structural optimizations (using a Γ-centered $5 \times 5 \times 5$ k-point mesh and an energy cutoff of 550 eV) of the lattice parameters and ionic positions, with both the Atou and dos Santos structures as our starting points. Both starting configurations converge to the same final structure, whose total energy is 0.25 eV per formula unit lower than the original dos Santos structure. Importantly, the relaxed structure is centrosymmetric with zero ferroelectric polarization; although the Bi^{3+} lone pairs lead to strong local polar distortions, the relative orientations of adjacent lone pairs are opposite to each other and equivalent, leading to an antiferroelectric arrangement (see Figure 1).

Therefore, our calculations suggest that the ground state of perovskite-structure $BiMnO_3$ is centrosymmetric with space group *C*2/*c* and zero ferroelectric polarization. Our result is robust to the computational parameters (we varied *U* between 0 and 10 eV and increased the volume up to 5% from our calculated optimized value) and consistent with recent experimental data on polycrystalline samples.[14] Note also that the LDA+*U* method used here has been shown to give structural properties that are in good agreement with experimental values for many transition metal oxides, including other multiferroics such as $BiFeO_3$.[29] We point out, however, that our calculations are for ideal, stoichiometric $BiMnO_3$, which might not always be achieved experimentally. We hope that our computations will motivate further work on $BiMnO_3$, in order to resolve the inconsistency between the apparently lower energy centrosymmetric structure and the reports of ferroelectric hysteresis[8] and second harmonic generation[9] which indicate noncentrosymmetry.

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